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URANIUM DIOXIDE

[1344-57-6]

Formula: UO_2 ; MW 270.03

Synonyms: uranium oxide; uranic oxide; urania; uranium(IV) oxide

Occurrence and Uses

Uranium dioxide occurs in nature as mineral uraninite. It is used in nuclear fuel rods for reactors. Also it is used in large incandescent lamps for photography or motion pictures and is connected to the tungsten filaments to prevent sudden surges of current.

Physical Properties

Brown to black powder or cubic crystals; density 10.97 g/cm^3 ; Mohs hardness 5.5; melts at $2,827^\circ\text{C}$; insoluble in water and dilute acids; soluble in concentrated acids.

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	-259.3 kcal/mol
$\Delta H_f^\circ(\text{gas})$	-111.3 kcal/mol
$\Delta G_f^\circ(\text{cry})$	-246.6 kcal/mol
$\Delta G_f^\circ(\text{gas})$	-112.7 kcal/mol
$S^\circ(\text{cry})$	18.4 cal/deg mol
$S^\circ(\text{gas})$	12.1 cal/deg mol
$C_p(\text{cry})$	15.2 cal/deg mol
$C_p(\text{gas})$	12.3 cal/deg mol

Preparation

Uranium dioxide occurs in mineral uraninite. Purified oxide may be obtained from uraninite after purification. The commercial material, however, also is recovered from other uranium sources. Uranium dioxide is obtained as an intermediate during production of uranium metal (See Uranium). Uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2$, obtained from digesting the mineral uraninite or pitchblende with concentrated nitric acid and separated by solvent extraction, is reduced with hydrogen at high temperatures to yield the dioxide.

Analysis

Elemental composition: U 88.15%, O 11.85%. The compound is digested in nitric acid and alpha activity is measured by a gas-flow proportional counter, alpha scintillation counter or other counting instrument.

Hazard

See Uranium.

URANIUM HEXAFLUORIDE

[7783-81-5]

Formula: UF_6 ; MW 352.02

Synonym: uranium(VI) fluoride

Uses

The compound is used in the gaseous diffusion process to separate uranium isotopes

Physical Properties

White monoclinic crystals; density 5.09 g/cm^3 ; melts at 64°C (triple point); sublimates at 56.6°C ; critical temperature 232.65°C ; critical pressure 46 atm; critical volume $250 \text{ cm}^3/\text{mol}$; reacts with water forming UO_2F_2 and HF ; soluble in chloroform, carbon tetrachloride and fluorocarbon solvents; soluble in liquid chlorine and bromine; dissolves in nitrobenzene to form a dark red solution that fumes in air.

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	-525.1 kcal/mol
$\Delta H_f^\circ(\text{gas})$	-513.2 kcal/mol
$\Delta G_f^\circ(\text{cry})$	-494.4 kcal/mol
$\Delta G_f^\circ(\text{gas})$	-493.2 kcal/mol
$S^\circ(\text{cry})$	54.4 cal/deg mol
$S^\circ(\text{gas})$	90.3 cal/deg mol
$C_p(\text{cry})$	39.9 cal/deg mol
$C_p(\text{gas})$	31.0 cal/deg mol
ΔH_{fus}	4.59 kcal/mol

Preparation

Uranium hexafluoride is prepared by the reaction of fluorine on uranium metal, triuranium octafluoride, uranium pentachloride, or uranium carbide.

One preparative method involves heating triuranium octaoxide, U_3O_8 , with hydrogen fluoride and fluorine. The product hexafluoride is separated and purified by fractional distillation.

Another preparative method involves converting triuranium octaoxide to uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2$, by treatment with nitric acid. Uranyl nitrate then is decomposed to uranium trioxide, UO_3 , which is reduced to the dioxide, UO_2 , with hydrogen. A fluidized bed of uranium dioxide is treated with hydrogen fluoride to produce uranium tetrafluoride, UF_4 , which then is treated with fluorine to form hexafluoride. The preparation should be done in copper apparatus.

Analysis

Elemental composition: U 67.62%, F 32.38%. The compound may be identified by its physical properties. Alpha activity may be measured by an alpha counter or an alpha spectrometer (See Uranium). Fluoride ion may be mea-

sured in an aqueous solution of the compound (reacts vigorously with water forming HF and UO_2F_2) by fluoride ion selective electrode or by ion chromatography.

Hazard

Uranium hexafluoride is a corrosive substance and also presents radiation hazard.

URANYL NITRATE

[10102-06-4]

Formula: $\text{UO}_2(\text{NO}_3)_2$; MW 394.04; exists as a stable hexahydrate

$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

[13520-83-7] MW 502.13

Synonyms: uranium oxynitrate; yellow salt

Uses

Uranyl nitrate is used to prepare several uranium salts. Also it is used to make uranium glaze and decorative porcelain, and as an intensifier in photography. It is an analytical reagent (e.g., Redox titration).

Physical Properties

The hexahydrate is a yellow crystalline solid; orthogonal crystals; density 2.81 g/cm^3 ; hygroscopic; melts at 60°C ; decomposes at 118°C ; very soluble in water; soluble in alcohol and ether.

Preparation

Uranyl nitrate is obtained as an intermediate in recovering uranium from its minerals. The compound can be prepared by reacting triuranium octaoxide, U_3O_8 , with nitric acid. It is separated and purified by extraction with ether.

Analysis

Elemental composition (anhydrous compound): U 60.41%, N 7.11%, O 32.48%. The compound may be identified by its physical properties and measured by gravimetric methods from its thermal decomposition to form uranium trioxide, UO_3 . The radioactivity may be measured by an alpha counter.

Hazard

The compound is toxic and presents a radiation risk.

VANADIUM

[7440-62-2]

Symbol V; atomic number 23; atomic weight 50.942; a Group V B (Group 5)

transition metal; electron configuration $[\text{Ar}]3d^34s^2$; valence states +2, +3, +4, +5; atomic radius 1.34Å; ionic radius V^{2+} , V^{3+} , V^{4+} , and V^{5+} are 0.79Å, 0.64Å, 0.58Å, and 0.54Å, respectively for CN 6; standard electrode potential, E° for $\text{V}^{2+} + 2e^- \leftrightarrow \text{V}$ is -1.175V ; two naturally-occurring isotopes: V-50 (0.25%), V-51 (99.75%); V-50 is radioactive with a $t_{1/2}$ of over 1.4×10^{17} year; sixteen artificial radioactive isotopes in the mass range 43-49, 52-60.

History, Occurrence, and Uses

Vanadium was discovered in 1801 by Mexican mineralogist Manuel del Rio in a lead ore in Hidalgo, Mexico. He named it *erythronium* because of the red color its salts when heated with acids. However, del Rio's discovery was mistakenly thought at that time to be a form of impure chromium. Swedish chemist Sefstrom in 1830 rediscovered this element detecting an unknown metal in the iron ores of Taberg, Sweden. He named it vanadium after the Scandinavian goddess Vanadis. Later in 1830, Wohler determined that del Rio's erythronium and Sefstrom's vanadium were the same element. Vanadium metal was prepared for the first time by Roscoe in 1867 in somewhat impure form, as a silvery-white powder, by reduction of vanadium chloride, VCl_2 , with hydrogen. Hunter and Jones in 1923 prepared the metal at 99.5% purity as a fine gray powder by thermal reduction of vanadium trichloride with sodium in a steel bomb.

Vanadium is found in several minerals including roscoelite, a vanadium-bearing mica $[2\text{K}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot (\text{Mg}, \text{Fe})\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 10\text{SiO}_2 \cdot 4\text{H}_2\text{O}]$; carnotite, $\text{K}_2\text{O} \cdot 2\text{U}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$; vanadinite, $9\text{PbO} \cdot 3\text{V}_2\text{O}_5 \cdot \text{PbCl}_2$; patronite, a polysulfide $\text{V}_2\text{S}_5 \cdot n\text{S}$; cuprodesclozite, $4(\text{Cu}, \text{Zn}, \text{Pb})\text{O} \cdot (\text{V}, \text{As})_2\text{O}_5 \cdot \text{H}_2\text{O}$; hewettite, $\text{CaO} \cdot 3\text{V}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$; and uvanite, $2\text{UO}_3 \cdot 3\text{V}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$. Also, it is found in phosphate rocks, many iron ores, and in some crude oils. Abundance in earth's crust is about 120mg/kg. Vanadium has been found in meteorites.

Vanadium is added to steel for high resistance to oxidation and to stabilize carbide. Vanadium foil is used for cladding titanium to steel. Vanadium-gallium alloy is used in making superconductive magnets. An important compound of vanadium is pentoxide which has many commercial uses (See Vanadium Pentoxide).

Physical Properties

A bright white metal; soft and ductile; body-centered cubic structure; index of refraction 3.03; density 5.96 g/cm³; melts at 1,910°C; vaporizes at 3,407°C; electrical resistivity, 18.1 microhm-cm at 0°C and 20.1 microhm-cm at 25°C; magnetic susceptibility 1.4×10^{-6} cgs units; modulus of elasticity $18\text{--}19 \times 10^6$ psi; shear modulus 6.73×10^6 psi; Poisson's ratio 0.36; thermal neutron absorption cross section 5 barns/atom; insoluble in water, dilute sulfuric acid, and hydrochloric acid at all concentrations; soluble in nitric acid, aqua regia, and concentrated sulfuric acid; insoluble in alkalis.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	122.9 kcal/mol

ΔG_f° (cry)	0.0 kcal/mol
ΔG_f° (gas)	180.3 kcal/mol
S° (cry)	6.91 cal/deg mol
S° (gas)	43.5 cal/deg mol
C_p (cry)	5.95 cal/deg mol
C_p (gas)	6.22 cal/deg mol
ΔH_{fus}	5.14 kcal/mol
Thermal Conductivity (at 27°C)	0.307 W/cm K
Coefficient of linear expansion (at 25°C)	$8.4 \times 10^{-6}/^\circ\text{C}$

Recovery

Vanadium is recovered from several sources; vanadium minerals, vanadium-bearing phosphates, boiler residues, and spent vanadium catalysts. One major vanadium mineral is patronite, a greenish-black, amorphous sulfide ore used extensively for many years to produce vanadium. This mineral, found in Peru, has depleted gradually. The metal also is recovered commercially from carnotite and roscoelite.

Vanadium usually is recovered from its ores by one of two processes, (1) leaching raw mineral with hot dilute sulfuric acid, and (2) roasting ore with common salt to convert vanadium into water soluble sodium vanadates. In the sulfuric acid leaching process, vanadium is extracted from acid leach liquors by solvent extraction with an aliphatic amine or an alkyl phosphoric acid in kerosene. The organic solvent extract then is treated with an aqueous solution of ammonia in the presence of ammonium chloride to convert vanadium into ammonium metavanadate. Alternatively, the organic extract is treated with dilute sulfuric acid or an aqueous solution of soda ash under controlled conditions of pH. Vanadium is precipitated from this solution as a red cake of sodium polyvanadate.

Alternatively, ore is roasted with common salt and the residue leached with water or sodium carbonate solution. To this aqueous solution of sodium vanadates, sulfuric acid is added and pH is adjusted between 2 and 3. Vanadate precipitates as a red cake of sodium polyvanadate.

The sodium polyvanadate obtained above by either method is decomposed thermally at 700°C producing a melt of vanadium pentoxide, V_2O_5 . Pentoxide obtained at this stage is in impure form. Purified vanadium pentoxide is obtained by dissolving the red cake in sodium carbonate solution to precipitate ammonium metavanadate. The metavanadate is decomposed at 320 to 430°C to form highly purified vanadium pentoxide.

Vanadium metal is prepared from pentoxide, V_2O_5 , by reduction with calcium at elevated temperatures. Presence of iodine lowers calcium reduction temperature to 425°C because of heat of formation of calcium iodide. Pentoxide also may be converted to the trichloride, VCl_3 , and the trichloride reduced with magnesium metal or magnesium-sodium mixture at high temperatures to form high purity ductile metal. Alternatively, a fused mixture of vanadium chloride, sodium chloride, and lithium chloride may be electrolyzed to produce the metal in high purity.

Reactions

Vanadium forms four oxides: the light grey monoxide, VO or (V₂O₂); the blue black dioxide, VO₂ (or V₂O₄); the black sesquioxide, V₂O₃; and the orange-red pentoxide, V₂O₅. The oxides are formed when the metal is heated in air or oxygen. Vanadium combines with chlorine on heating. Three chlorides are known: the green dichloride, VCl₂; the pink trichloride, VCl₃; and the brown-red tetrachloride, VCl₄. The more stable tetrachloride is formed when the metal is heated with chlorine at 180°C. The metal also forms three fluorides in valence states +3, +4, and +5. They are the green trifluoride, VF₃; a yellowish-brown tetrafluoride, VF₄, and the white pentafluoride, VF₅. When heated with bromine vapor vanadium forms the green-black tribromide, VBr₃. Vanadium forms two iodides, a violet-rose diiodide, VI₂, and a deliquescent triiodide, VI₃.

Vanadium combines with other nonmetals at elevated temperatures forming binary compounds. Such compounds include nitride, VN; carbide VC, and the sulfides, VS (or V₂S₂), V₂S₃, and V₂S₅.

Vanadium reacts with fused caustic soda and caustic potash to form water soluble vanadates with liberation of hydrogen. The metal, however, is stable in alkaline solutions.

Analysis

Trace quantities of vanadium in solid materials or water can be measured by flame-AA or ICP-AES methods. For such analysis the metal or its compounds or alloys have to be dissolved by digestion with nitric acid or aqua regia. Flame-AA measurement may be made at 318.4 nm using a nitrous oxide-acetylene flame. ICP-AES measurement may be made at 292.40nm. Other wavelengths may be substituted. Vanadium ions in solution can be measured by colorimetry using a spectrophotometer or a filter photometer at 415 nm. Color formation is based on catalytic effect of vanadium on reaction of gallic acid with persulfate ion in acid solution. An ammonium persulfate-phosphoric acid reagent solution may be used in the test. Many metal ions and halide ions may interfere in the test.

VANADIUM PENTOXIDE

[1314-62-1]

Formula V₂O₅; MW 181.88

Synonyms: vanadium(V) oxide; vanadic acid anhydride; vanadic anhydride.

Uses

The most important applications of vanadium pentoxide are in catalysis. It is a catalyst in manufacturing sulfuric acid by contact process. Also, it catalyzes conversion of ethanol to acetaldehyde, and many organic reactions. Other applications are in making yellow glass; as a depolarizer; as a developer in photography; inhibiting UV transmission in glass; and coloring ceram-

ics. Vanadium pentoxide is used to prepare many vanadium compounds including ammonium vanadate used in making aniline black dye, and as a mordant for dyeing and printing fabrics.

Physical Properties

Brown-yellow orthorhombic crystals; density 3.35 g/cm³; melts at 670°C; decomposes at 1,800°C; slightly soluble in water, 0.8g/100 mL at 20°C; soluble in concentrated acids forming an orange-yellow solution; soluble in alkalis forming vanadates.

Thermochemical Properties

ΔH_f°	-370.6 kcal/mol
ΔG_f°	-339.3 kcal/mol
S°	31.3 cal/deg mol
C_p	30.5 cal/deg mol
ΔH_{fus}	15.4 cal/deg mol

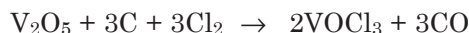
Preparation

Vanadium pentoxide is an intermediate in recovering vanadium from minerals (See Vanadium). Sodium polyvanadate, obtained as a red cake in one of the steps in extracting vanadium from its ores is calcined at 700°C in air to form a melt of vanadium pentoxide. Pentoxide is prepared in purified form by dissolving red cake in sodium carbonate solution followed by addition of an aqueous solution of ammonia and ammonium chloride. Ammonium metavanadate is precipitated which on decomposition at 320 to 430°C forms vanadium pentoxide.

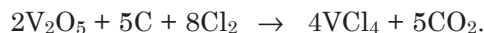
Reactions

Vanadium pentoxide may be reduced to vanadium tetraoxide, trioxide, or vanadium metal by various reducing agents including hydrogen, carbon, and oxalic acid. Pentoxide may be reduced to metal by heating at high temperatures with calcium or magnesium.

Pentoxide when heated with chlorine gas at 500°C in the presence of carbon forms vanadium oxytrichloride:



At a higher temperature of 750°C vanadium tetrachloride is produced:

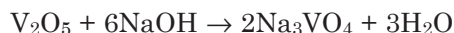
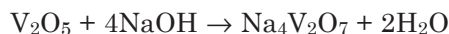
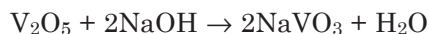


When sulfur dioxide is passed through a solution of vanadium pentoxide in sulfuric acid, the product is blue crystalline vanadyl sulfate:



Vanadium pentoxide reacts with caustic soda to form a series of water-sol-

uble vanadates: sodium metavanadate, NaVO_3 , sodium pyrovanadate, $\text{Na}_4\text{V}_2\text{O}_7$, and sodium orthovanadate, Na_3VO_4 . The specific product depends on molar proportions of caustic soda:



Analysis

Elemental composition: V 56.02%, O 43.98%. An acid solution is analyzed for vanadium (See Vanadium). Pentoxide in sulfuric acid may be converted to vanadyl sulfate by reduction with SO_2 (See Reactions) or ferrous ammonium sulfate (FAS). The excess FAS may be destroyed with ammonium persulfate. Vanadyl sulfate is then titrated with a standard solution of potassium permanganate:



Toxicity

The compound is toxic by ingestion, inhalation, and contact. Inhalation can cause asthma, cough, dyspnea, and bronchial constriction. Ingestion can cause gastrointestinal tract disturbances. Other toxic symptoms are skin pallor, greenish-black tongue, and papular skin rash (Lewis, R.J. (Sr) 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold).

The oral LD_{50} for V_2O_5 dust in rats is 10 mg/kg and the inhalation LC_{LO} in rats is 70 $\text{mg}/\text{m}^3/2\text{hr}$.

VANADYL SULFATE

[27774-13-6]

Formula VOSO_4 ; MW 163.00; exists as a dihydrate, $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$.

Synonym: vanadium oxysulfate

Uses

The dihydrate is a mordant in dyeing and printing fabrics; used in preparing aniline black; a colorant in ceramics to form blue and green glazes; used in making colored glass; and a reducing agent.

Physical Properties

The dihydrate, $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ is a blue black crystalline powder, soluble in water.

Preparation

Vanadyl sulfate is prepared by passing sulfur dioxide through a cold solution of vanadium pentoxide in sulfuric acid, followed by crystallization:



Analysis

Vanadyl sulfate may be analyzed by titration with a standard solution of potassium permanganate (See Vanadium Pentoxide, Analysis) or any suitable oxidizing agent. An aqueous solution may be analyzed for vanadium by AA or ICP (See Vanadium).

WATER

[7732-18-5]

Formula H_2O ; MW 18.015; bent molecule; H–O–H bond angle 104.5° ; H–O bond distance $0.9575 \text{ \AA}$; bond dissociation energy of O–H bond 101.2 kcal/mol ; intermolecular force: hydrogen bonding

Uses

Water is among the most important compounds on earth. It is the main constituent of the hydrosphere, which along with the mantle, crust, and the atmosphere are the four components of our planet. It is present everywhere on earth and is essential for sustenance of life. Water also determines climate, weather pattern, and energy balance on earth. It also is one of the most abundant compounds. The mass of all water on earth is $1.4 \times 10^{21} \text{ kg}$ and the total volume is about $1.4 \times 10^9 \text{ km}^3$, which includes 97.20% of salt water of oceans, 2.15% of fresh water in polar ice caps and glaciers, 0.009% in freshwater lakes, 0.008% in saline lakes, 0.62% as ground waters, 0.005% in soil moisture; 0.0001% in stream channels and 0.001% as vapors and moisture in the atmosphere.

Among the major industrial applications of water are generation of hydroelectric power, steam generation, industrial solvent, diluent, moderator in nuclear reactions, industrial coolant, washing and cleaning, textile processing, preparation of food and beverages, filtration processes, and generation of hydrogen by electrolysis. Also, water provides the aqueous phase to carry out innumerable chemical reactions in the production of myriads of chemical substances including mineral acids, alkalies and their salts.

Physical Properties

Colorless, odorless, tasteless liquid; refractive index 1.3330; exists in three allotropic forms: solid ice, liquid water, and gaseous steam (or vapor); density of water increases with temperature, becomes maximum 1.0000 g/mL at 3.98°C and then decreases with rise in temperatures; density at 25°C 0.997 g/cm^3 ; density of water at 100°C 0.9584 g/mL ; density of steam 0.000596 g/mL at 100°C .

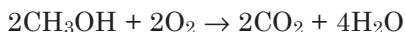
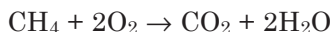
Water freezes to ice at 0°C; expands by about 10% on freezing; boils at 100°C; vapor pressure at 0°, 20°, 50°, and 100°C are 4.6, 17.5, 92.5, and 760 torr, respectively; dielectric constant 80.2 at 20°C and 76.6 at 30°C; dipole moment in benzene at 25°C 1.76; critical temperature 373.99°C; critical pressure 217.8 atm; critical density 0.322 g/cm³; viscosity 0.01002 poise at 20°C; surface tension 73 dynes/cm at 20°C; dissolves ionic substances; miscible with mineral acids, alkalis; low molecular weight alcohols, aldehydes and ketones; forms an azeotrope with several solvents; immiscible with nonpolar solvents such as carbon tetrachloride, hexane, chloroform, benzene, toluene, and carbon disulfide.

Thermochemical Properties

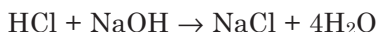
ΔH_f° (liq)	-68.32 kcal/mol
ΔH_f° (gas)	-57.80 kcal/mol
ΔG_f° (liq)	-56.69 kcal/mol
ΔG_f° (gas)	-54.63 kcal/mol
S° (liq)	16.71 cal/deg mol
S° (gas)	45.10 cal/deg mol
C_p (liq)	17.99 cal/deg mol
C_p (gas)	8.025 cal/deg mol
ΔH_{fus}	1.436 kcal/mol
ΔH_{vap}	9.716 kcal/mol

Production

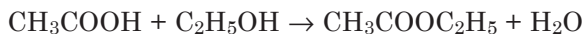
Water is produced by combustion of hydrogen with oxygen at high temperatures in the presence of a catalyst. Also, all combustion reactions of hydrocarbons (C, H compounds) or oxygenated hydrocarbons (C, H, O) yield water and carbon dioxide:



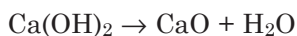
All acid-base neutralization reactions form water:



Organic condensation reactions eliminate a water molecule:



Many hydroxides dehydrate at high temperatures forming oxides and water:



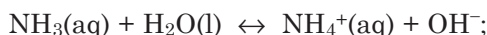
Water can be purified by distillation, ion exchange, filtration, carbon adsorption, and chlorination.

Reactions

Water undergoes autoionization to a small extent; the ionization constant at 25°C is 1.008×10^{-14} :



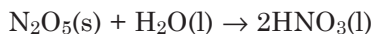
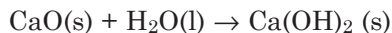
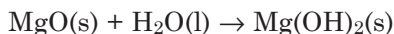
Water reacts both as an acid and a base. With bases it reacts as an acid:



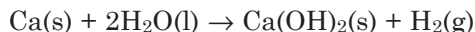
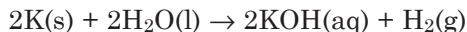
and with acids it reacts as a base:



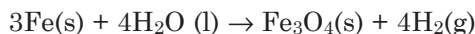
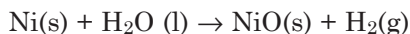
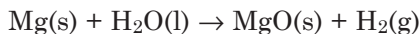
Water reacts with many metal oxides and nonmetal oxides forming bases and acids, respectively:



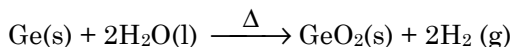
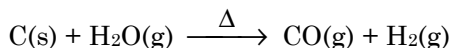
Water also behaves both as an oxidizing and reducing agent. With alkali and alkaline earth metals, which are strong reducing agents, water acts as an oxidizing agent. Reactions occur violently or vigorously at ambient temperatures with all alkali metals and calcium, strontium, and barium forming their hydroxides with liberation of hydrogen:



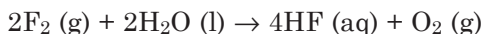
With less active metals, reactions occur at high temperatures. In such reactions oxides are formed instead of hydroxides, liberating hydrogen:



Water reacts with nonmetals and metalloid elements at very high temperatures forming oxides:



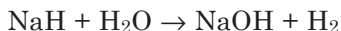
Water behaves as a reducing agent in reactions with oxidizing agents:



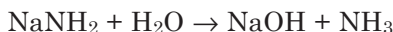
Water reacts with carbon monoxide at high temperatures (200 to 400°) in the presence of a catalyst to yield carbon dioxide and hydrogen. The reaction also is known as water-gas shift reaction:



Water reacts with metal hydrides liberating hydrogen. With the hydrides of sodium and potassium the reaction progresses with explosive violence:



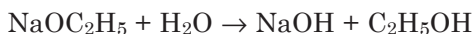
With alkali metal amides violent reactions occur, forming alkali hydroxides and ammonia:



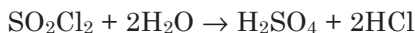
Violent reactions occur with lithium aluminum hydride and similar compounds:



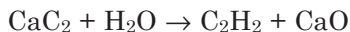
Sodium ethoxide decomposes in water forming sodium hydroxide and ethanol:



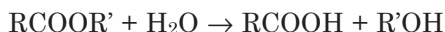
Sulfuryl chloride, SO_2Cl_2 , reacts with ice-cold water to form a hydrate, $\text{SO}_2\text{Cl}_2 \cdot 15\text{H}_2\text{O}$. However, at ambient temperature water decomposes sulfuryl chloride slowly forming sulfuric acid and hydrochloric acid:



Water reacts with calcium carbide to form acetylene:



Water forms hydrates with a large number of metal salts. Such hydrates are formed from absorption of moisture from air by anhydrous salts. Examples are $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. In many salt hydrates, water molecules coordinate to the metal ions, e.g., $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2$. Organic esters are hydrolyzed to form corresponding organic acids and alcohol. The reaction is catalyzed by acids:



Analysis

Water can be identified from its physical properties. Also, trace amounts of water may be determined by Karl-Fischer analysis. The Karl-Fisher reagent is a solution of iodine, sulfur dioxide and pyridine in methanol or methyl cellosolve. Water of crystallization in hydrates can be measured by TGA and DTA methods. The presence of trace moisture in gases can be determined by mass spectrometry. The characteristic mass ion is 18.

XENON

[7440-63-3]

Symbol Xe; atomic number 54; atomic weight 131.29; a noble gas; a Group VIII A (Group 18) inert gas element; electron configuration $[\text{Kr}]4\text{d}^{10}5\text{s}^25\text{p}^6$; valence, usually 0, but known to form compounds with fluorine and oxygen; atomic radius 1.31Å; nine naturally-occurring stable isotopes: Xe-124(0.10%), Xe-126 (0.09%), Xe-128(1.91%), Xe-129(26.46%), Xe-130(4.11%), Xe-131(21.24%), Xe-132(26.95%), Xe-134(10.42%), Xe-136(8.91%); twenty-seven artificial radioactive isotopes in the mass range 110-123, 125, 127, 133, 135, 137-145; longest-lived radioisotope Xe-127, $t_{1/2}$ 36.4 days; shortest-lived radioisotope Xe-110, $t_{1/2}$ 0.2 second.

History, Occurrence, and Uses

Xenon was discovered by Ramsay and Travers in 1898 while purifying krypton by fractional distillation. The name is from the Greek word *zenos* meaning "Stranger."

Xenon occurs in the atmosphere at trace concentrations. It also occurs in gases from certain mineral springs. Xenon also is a fission product of uranium, plutonium, and thorium isotopes induced by neutron bombardment. The radioactive fission product, xenon-135, has a very high thermal neutron cross-section. The element has been detected in Mars' atmosphere.

Xenon is a filling gas for light bulbs in high-intensity lamps and in flash lamps for photography. It forms a beautiful blue glow under vacuum in an electric discharge tube. It also is used in lamps that excite ruby lasers to produce coherent light. Xenon gas is a filler in proportional radiation counters and liquid xenon bubble chambers. Xenon is an anesthetic gas in surgery.

Radioactive xenon is a biological tracer.

Physical Properties

Colorless, odorless, tasteless gas; density of the gas 5.761 g/L at STP; heavier than air, about 4.5 times heavier than air (air=1); liquefies at -108.04°C ; density of liquid xenon 3.52 g/mL at its boiling point; freezes to a solid at -111.75°C ; density of solid xenon 2.7 g/cm³ at -140°C ; critical pressure 57.64 atm; critical temperature 16.058°C ; critical volume 118 cm³/mol; solubility in water 203.2 mL/L at STP and 108.1 mL/L at 20°C .

Thermochemical Properties

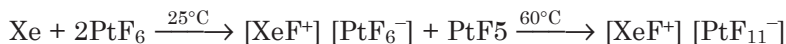
ΔH_f°	0.0
ΔG_f°	0.0
S°	40.5 cal/deg mol
C_p	4.97 cal/deg mol
Thermal conductivity	5.5 mW/mK
ΔH_{fus}	1.436 kcal/mol
ΔH_{vap}	3.02 kcal/mol

Production

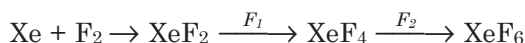
Xenon is recovered from air by liquefaction and fractional distillation. Usually it is obtained as a by-product of making other noble gases. It is collected in the liquid oxygen fraction along with krypton, acetylene, and other hydrocarbons that may be present in air. The xenon fraction is flash vaporized. Hydrocarbons present are separated by burning over a catalyst. Xenon is absorbed on silica gel at low temperatures. Finally, it is separated from krypton by selective absorption and desorption from charcoal.

Compounds

Although xenon has the stable octet configuration and is thought to be as inert as other noble gases, several xenon compounds have been prepared. The first xenon compound synthesized by N. Bartlett in 1962 was a red solid, XePtF₆, made by the reaction of xenon with platinum hexafluoride undergoing the following oxidation sequence (Cotton, F. A., Wilkinson G., Murillo, C. A. and M. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed., pp. 588. New York: John Wiley & Sons):



Xenon forms three binary fluorides, XeF₂, XeF₄, and XeF₆. Fluorine is the only element with which xenon reacts directly forming XeF₂. Reactions occur with excess xenon under pressure:



Bartlett prepared xenon difluoride by the reaction of xenon with silver fluoride in hydrofluoric acid in the presence of boron trifluoride:



Xenon tetrafluoride also can be prepared by oxidizing xenon with dioxygen difluoride, O_2F_2 , or by photolysis of xenon-fluorine mixture.

All other compounds of xenon are made from xenon fluorides.

Compounds in oxidation states +2, +4, +6, and +8 are well known. The tetrafluoride and hexafluoride are readily hydrolyzed by water forming xenon trioxide, XeO_3 , and the xenon tetraoxide, XeO_4 , both of which are dangerously explosive. While the trioxide XeO_3 is a colorless crystalline solid, stable in solution, the tetraoxide XeO_4 is a colorless unstable gas.

The oxyfluoride, XeOF_4 is a stable colorless liquid produced by the reaction of xenon hexafluoride with sodium nitrate:



The oxodifluoride, XeOF_2 , dioxodifluoride, XeO_2F_2 and the trioxodifluoride, XeO_3F_2 all are unstable.

Xenon also forms many fluoroanions and their salts, mostly prepared from xenon tetrafluoride and hexafluoride. Such compounds include $\text{Na}^+\text{XeF}_5^-$ and $\text{Cs}^+\text{XeF}_7^-$ formed by reactions of xenon fluorides with sodium fluoride or cesium fluoride. The dicesium xenon octafluoride, Cs_2XeF_8 , is a stable yellow solid that decomposes above 400°C .

Analysis

Xenon can be identified by GC-TCD or by the GC/MS. The latter is a confirmatory test. The mass ions for its identification are 132, 129, 131, 134, 136, and 130 in the order of abundance corresponding to xenon isotopes.

YTTERBIUM

[7440-64-4]

Symbol Yb; atomic number 70; atomic weight 173.04; a lanthanide series rare earth metal; electron configuration $[\text{Xe}]4f^{14}6s^2$; valence +2, +3; atomic radius 1.945Å; ionic radius, Yb^{3+} 0.868Å and 0.98Å for CN 6 and 8; respectively; standard electrode potential, E° for $\text{Yb}^{3+} + 3e^- \leftrightarrow \text{Yb}$ is -2.19V ; seven naturally-occurring stable isotope: Yb-170 (3.05%), Yb-171 (14.32%), Yb-172 (21.93%), Yb-173 (16.12%), Yb-174 (31.84%), Yb-176 (12.72%); twenty-three artificial radioactive isotopes in the mass range 151-167, 169, 175, 177-180; the longest-lived radioisotope Yb-169, $t_{1/2}$ 32.03 days; shortest-lived radioisotope Yb-154, $t_{1/2}$ 0.40 second.

History, Occurrence, and Uses

Ytterbium was discovered in 1878 by J. C. G. de Marignac. He found a new component ytterbia in supposedly pure erbia or erbium oxide that had been

isolated earlier by Mosander. The element got its name from the Swedish village Ytterby where this rare earth first was found. Urbain in 1907 separated ytterbia into two components, neoytterbia and lutecia, that are oxides of ytterbium and lutecium respectively. These two elements were discovered independently by von Welsbach around the same time. Klemm and Bommer in 1937 first prepared metallic ytterbium by reduction with potassium. The metal they prepared was impure, mixed with potassium chloride. Pure metal was prepared first by Daane, Dennison, and Spedding in 1953 in gram quantities.

Ytterbium occurs in minerals euxenite, a complex titanium niobotantalate; gadolinite, a rare earth iron beryllium silicate; monazite, a thorium-rare earth phosphate; and xenotime, also a rare earth-thorium phosphate. Abundance of ytterbium in the earth's crust is estimated to be 3.2 mg/kg.

The metal has very little commercial use. In elemental form it is a laser source, a portable x-ray source, and as a dopant in garnets. When added to stainless steel, it improves grain refinement, strength, and other properties. Some other applications, particularly in oxides mixed with other rare earths, are as carbon rods for industrial lighting, in titanate insulated capacitors, and as additives to glass. The radioactive isotope ytterbium-169 is used in portable devices to examine defects in thin steel and aluminum. The metal and its compounds are used in fundamental research.

Physical Properties

Silvery lustrous metal; soft, malleable and ductile; the metal exists in two allotropic forms: an alpha form, which has a face-centered cubic structure and is stable at room temperature, and a beta form, a body-centered cubic modification that forms when the alpha form is heated to 798°C. Density of the alpha modification is 6.98 g/cm³ and that of beta form is 6.54 g/cm³. Alpha phase exhibits metallic-type conductivity at ordinary temperatures and pressures, but becomes semi-conductive above 16,000 atm. At about 40,000 atm it again becomes metallic-type conductor. (In some texts, the term beta form refers to the alpha phase).

Ytterbium melts at 824°C; vaporizes at 1,194°C; electrical resistivity 25.0 microhm-cm; Vickers hardness 21 kg/mm²; Young's modulus 0.182x10⁻⁶ kg/cm²; shear modulus 0.071x10⁻⁶ kg/cm²; Poisson's ratio 0.284; magnetic susceptibility 71x10⁶ emu/mol; thermal neutron absorption cross section 37 barns; reacts slowly with water; soluble in dilute acids and ammonia.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	36.4 kcal/mol
ΔG_f° (gas)	28.3 kcal/mol
S° (cry)	14.3 cal/deg mol
S° (gas)	41.4 cal/deg mol
C_p (cry)	6.38 cal/deg mol
C_p (gas)	4.97 cal/deg mol
ΔH_{fus}	1.83 kcal/mol

Thermal Conductivity (at 27°C)	0.385 W/cm K
Coefficient of linear expansion(at 25°C)	26.3x10 ⁻⁶ /°C

Recovery

Recovery of ytterbium from ores involves several processes that are mostly common to all lanthanide metals. These are discussed individually under each rare earth metal. Recovery involves three major steps: (1) processing of ores, (2) separation of ytterbium from rare earth mixtures, and (3) preparation of the metal.

If the starting material is gadolinite, ore is digested with hydrochloric or nitric acid. Rare earths dissolve in acid. The solution is treated with sodium oxalate or oxalic acid to precipitate rare earths as oxalates. For euxenite, ore is opened either by fusion with potassium bisulfate or digestion with hydrofluoric acid. If monazite or xenotime is extracted, ore is either heated with sulfuric acid or digested with caustic soda solution at elevated temperatures.

Various processes separate rare earths from other metal salts. These processes also separate rare earths into specific subgroups. The methods are based on fractional precipitation, selective extraction by nonaqueous solvents, or selective ion exchange. Separation of individual rare earths is the most important step in recovery. Separation may be achieved by ion exchange and solvent extraction techniques. Also, ytterbium may be separated from a mixture of heavy rare earths by reduction with sodium amalgam. In this method, a buffered acidic solution of trivalent heavy rare earths is treated with molten sodium mercury alloy. Yb³⁺ is reduced and dissolved in the molten alloy. The alloy is treated with hydrochloric acid, after which ytterbium is extracted into the solution. The metal is precipitated as oxalate from solution.

After separation from other rare earths, ytterbium is usually obtained as its oxide, Yb₂O₃. If separated as oxalate, oxalate is converted into oxide by high temperature. Ytterbium oxide is reduced to metallic ytterbium by heating with lanthanum metal in high vacuum. The metal is purified by sublimation and collected over a condenser plate. Aluminum, zirconium, and cerium also are effective reducing agents and may be used instead of lanthanum.

Reactions

Ytterbium reacts with oxygen above 200°C. It forms two oxides, the monoxide, YbO, and more stable sesquioxide, Yb₂O₃.

The metal dissolves in dilute and concentrated mineral acids. Evaporation crystallizes salts. At ordinary temperatures, ytterbium, similar to other rare earth metals, is corroded slowly by caustic alkalies, ammonium hydroxide, and sodium nitrate solutions. The metal dissolves in liquid ammonia forming a deep blue solution.

Reactions with halogens are slow at room temperature but progress rapidly above 200°C forming ytterbium trihalides. All the trihalides; namely, the YbCl₃, YbBr₃, and YbI₃ with the exception of trifluoride, YbF₃, are hygroscopic and soluble in water.

Ytterbium forms many binary, metalloid, and intermetallic compounds with a number of elements when heated at elevated temperatures. When

heated with hydrogen, nitrogen, sulfur, and carbon at high temperatures, the corresponding binary compounds are produced.

Analysis

The metal can be analyzed by flame-AA and ICP-AES methods. Ytterbium or its compounds are dissolved by acid digestion and diluted before such analysis. X-ray methods and neutron activation analysis are also applicable.

YTTERBIUM OXIDE

[1314-37-0]

Formula Yb_2O_3 ; MW 394.08

Synonyms: ytterbium (III) oxide; ytterbia

Uses

Ytterbium oxide is used in cored carbon rods for industrial lighting. The oxide also is used as an additive in special glasses. Other uses are in dielectric ceramics and special alloys.

Physical Properties

Colorless cubic crystals when pure; tinted brown or yellowish white in presence of thulia; density 9.2 g/cm^3 ; melts at $2,435^\circ\text{C}$; insoluble in water; soluble in hot dilute acids.

Thermochemical Properties

ΔH_f°	-433.7 kcal/mol
ΔG_f°	-412.7 kcal/mol
S°	31.8 cal/deg mol
C_p	27.6 cal/deg mol

Production

Ytterbium oxide is produced as an intermediate in recovering ytterbium from minerals (See Ytterbium). After opening the ore by digestion with concentrated sulfuric acid or caustic soda solution at high temperatures, rare earths are separated by ion exchange, solvent extraction, or fractional precipitation. Ytterbium fraction is treated with oxalic acid or sodium oxalate to precipitate ytterbium oxalate, which is ignited to yield ytterbium oxide.

Analysis

Elemental composition: Yb 87.82%, O 12.18%. Ytterbium oxide is dissolved in dilute acids and diluted for analysis by flame-AA or ICP-AES methods. The oxide may be characterized by x-ray.

YTTRIUM

[7440-65-5]

Symbol Y; atomic number 39; atomic weight 88.906; a Group III B (Group 3 transition metal; electron configuration [Kr]4d¹5s²; valence +3; atomic radius 1.80Å; standard electronic potential, E° for $Y^{3+} + 3e \leftrightarrow Y$ is -2.372 V; one naturally-occurring stable isotope, Y-89 (100%); twenty-four artificial radioactive isotopes in the mass range 78-88, 90-102; the longest-lived radioisotope; Y-88, $t_{1/2}$ 106.6 days; shortest-lived radioisotope Y-98, $t_{1/2}$ 0.59 second.

History, Occurrence, and Uses

The element was discovered in 1794 by the Swedish chemist Gadolin. He named it after the small town Ytterby in Sweden where the mineral containing yttria was found. Mosander in 1843 determined that the yttria consisted of three oxides: yttria, erbia, and terbia. Yttrium occurs in all rare earths. It is recovered commercially from monazite sand, which contains about 3% yttrium. It also is found in bastnasite in smaller amounts of about 0.2%. Abundance of yttrium in earth's crust is estimated to be 33 mg/kg. The metal has been detected in moon rocks.

Yttrium alloys have many applications. The metal doped with rare earths such as europium is used as phosphor for color television receivers. When added to iron, chromium, vanadium, niobium, and other metals it enhances resistance of these metals and their alloys to high temperature oxidation and recrystallization. It is a deoxidizer for vanadium and other nonferrous metals. Yttrium-aluminum garnets are used in lasers and in jewelry gemstones. Yttrium-iron garnets are used as transmitters and as transducers of acoustic energy.

Physical Properties

Grayish lustrous metal; darkens when exposed to light; hexagonal close-packed crystals converting to body-centered cubic structure at 1,490°C; density 4.469 g/cm³ at 25°C; Brinell hardness 32; melts at 1,526°C; vaporizes at 3,336°C; electrical resistivity 59.6 microhm-cm at 25°C; compressibility 2.09×10^{-6} cm²/kg; Young's modulus 9.62×10^6 psi; Poisson's ratio 0.265; reacts with water; soluble in dilute acids and alkalis.

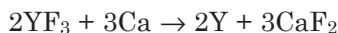
Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	100.7 kcal/mol
ΔG_f° (gas)	91.1 kcal/mol
S° (cry)	10.6 cal/deg mol
S° (gas)	42.9 cal/deg mol
C_p (cry)	6.19 cal/deg mol
C_p (gas)	6.38 cal/deg mol
ΔH_{fus}	2.72 kcal/mol
Thermal Conductivity (at 27°C)	0.172 W/cm K
Coefficient of linear expansion (at 25°C)	$10.6 \times 10^{-6}/^\circ\text{C}$

Recovery

Yttrium is recovered commercially from its two principal sources, xenotime and monazite. Ore is opened by digestion with hot sulfuric acid. Insoluble residues are filtered out and leachate solution containing yttrium and other rare-earths is loaded onto cation exchange resin beds for separation. Fractions are eluted with ethylenediamine tetraacetic acid (EDTA) buffered with ammonia at varying temperatures. Also, many other chelates are highly effective in eluting rare earths. Such temperature adjustments of resin beds enhance separation efficiency, particularly for separating yttrium. Separated rare earths including yttrium are converted into insoluble oxalates that precipitate when treated with oxalic acid or sodium oxalate.

Yttrium oxalate is then ignited to its oxide, Y_2O_3 . The oxide is heated at $750^\circ C$ in a stream of anhydrous hydrogen fluoride to yield yttrium fluoride, YF_3 . Alternatively, the oxide is mixed with ammonium hydrogen fluoride NH_4HF_2 and heated at $400^\circ C$ in a stream of dry air or helium. Yttrium metal may be produced from its fluoride either by metallothermic reduction or electrolysis. The more common metallothermic reduction involves reducing the fluoride with redistilled calcium in 10% excess over the stoichiometric amounts at elevated temperatures:



In the electrolytic process, a fused bath of yttrium fluoride and lithium fluoride is heated to nearly $1,700^\circ C$ and electrolyzed. The electrolysis is done in a graphite crucible using molybdenum cathodes at which yttrium is produced as molten metal.

Yttrium is purified by distillation at high temperatures under vacuum.

Reactions

The chemical properties of yttrium are more similar to those of rare earths than to scandium. However, unlike the rare earths, yttrium exhibits only one valence state, +3.

Yttrium combines with oxygen forming its only oxide, Y_2O_3 . The reaction is much faster at high temperatures, particularly above $400^\circ C$. The metal, in the form of sponge or small particles, can ignite at this temperature. At ambient temperature the metal is slightly tarnished by oxygen or air, forming a very thin film of oxide that protects the metal from further oxidation.

Yttrium reacts with water vapor at high temperatures, usually above $750^\circ C$, forming a protective oxide coating.

The metal reacts with halogens above $200^\circ C$ forming its trihalides. It combines with nitrogen above $1,000^\circ C$ producing a nitride, YN . It combines at elevated temperatures forming binary compounds with most nonmetals and some metalloid elements such as hydrogen, sulfur, carbon, phosphorus, silicon, and selenium.

Analysis

The metal or its compounds can be analyzed at trace levels by flame-AA,

ICP-AES, ICP/MS and neutron activation. ICP/MS is the most sensitive method. The metal is dissolved by acid digestion and diluted prior to analysis.

YTTRIUM OXIDE

[1314-36-9]

Formula Y_2O_3 ; MW 225.81

Synonym: yttria

Uses

The oxide is used in phosphors that form red color in color television tubes. Also, it is used in gas mantles and acetylene lights. Other uses are in yttrium-iron garnets for microwave filters in lasers, and as a stabilizer for high temperature in refractories.

Physical Properties

White powder; body-centered cubic structure; density 5.03 g/cm³; melts at 2,436°C; insoluble in water; soluble in dilute acids.

Thermochemical Properties

ΔH_f°	-455.4 kcal/mol
ΔG_f°	-434.2 kcal/mol
S°	23.7 cal/deg mol
C_p	24.5 cal/deg mol
ΔH_{fus}	25.1 kcal/mol

Preparation

Yttrium oxide is produced as an intermediate in recovery of yttrium from xenotime and monazite (See Yttrium, Recovery). The oxide is produced after separation of rare earth sulfates obtained from digesting the mineral with sulfuric acid on a cation exchange bed, precipitating yttrium fraction as oxalate, and igniting the oxalate at 750°C.

Yttrium oxide also may be obtained by thermal decomposition of yttrium nitrate.

Analysis

Elemental composition: Y 78.74%, O 21.26%. Oxide is dissolved in nitric acid and the solution analyzed for yttrium (See Yttrium). Oxide may be characterized by x-ray diffraction.

YTTRIUM SULFATE

[7446-33-5]

Formula $\text{Y}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$; MW 610.125; prepared and sold as octahydrate

Uses

Yttrium sulfate is used in making many yttrium salts.

Physical Properties

Red monoclinic crystals; density 2.59 g/cm³; loses all its water molecules at 120°C; decomposes at 700°C; sparingly soluble in water, less soluble in hot water; dissolves in concentrated sulfuric acid forming Y(HSO₄)₃; insoluble in alkalis; forms double salts with alkali sulfates.

Preparation

Yttrium sulfate is produced as an intermediate in recovering yttrium from monazite or xenotime (see Yttrium, Recovery). Rare earth sulfates are separated on a cation exchange resin bed. Yttrium fraction is purified by fractional crystallization. Alternatively, yttrium sulfate may be prepared by reacting yttrium oxide with sulfuric acid.

Analysis

Water of crystallization may be measured by thermogravimetric analysis. The compound is dissolved in concentrated sulfuric acid, diluted, and analyzed for yttrium by flame-AA or ICP-AES.

ZINC

[7440-66-6]

Symbol Zn; atomic number 30; atomic weight 65.39; a Group II B (Group 12) metallic element; electron configuration [Ar]3d¹⁰4s²; valence +2; atomic radius 1.34Å; ionic radius 0.60Å (CN 4) and 0.74Å (CN 6); standard electrode potential, E° for Zn²⁺ + 2e⁻ ↔ Zn is -0.7618 V; five naturally-occurring isotopes: Zn-64 (48.63%), Zn-66 (27.92%), Zn-67 (4.11%), Zn-68 (18.84%), Zn-70(0.61%); nineteen artificial radioactive isotopes in the mass range 57, 59-63, 65, 69, 71-81; the longest-lived radioisotope, Zn-65, t_{1/2} 243.8 days; shortest-lived radioisotope, Zn-57, t_{1/2} 0.04 second.

History, Occurrence, and Uses

Zinc is another earliest known metal. Use of its alloy, brass, dates back to prehistoric times. The metal was produced in India in the 13th century by reducing calamine (a silicate mineral of zinc) with wool. Marggraf produced the metal in 1746 by reducing calamine with charcoal. The element took its name from the German word *zink* meaning "of obscure origin." Lohneyes first used this name in 1697.

Zinc occurs in nature, widely distributed. The principal ores are sphalerite (and wurtzite) known as zinc blende, ZnS; gahnite, ZnAl₂O₄; calamine; smithsonite, ZnCO₃; franklinite, ZnFe₂O₄; and zincite, ZnO. Abundance in earth's crust is about 70 mg/kg and average concentration in sea water is about 10 µg/L.

Some important applications of zinc include galvanizing steel; to produce die castings; as a chemical additive in rubber and paints; in dry cells; in making electrodes; and as a reducing agent. Steel is galvanized by a thin coating of zinc to protect it from corrosion. Such galvanized steel is used in buildings, cars, and appliances. High-purity zinc is alloyed with aluminum at varying compositions, along with small amounts of copper and magnesium, to produce die castings. Such die castings are used extensively in automotive, hardware, and electrical industries. Zinc forms numerous alloys including brass, nickel silver, German silver, commercial bronze, soft solder, aluminum solder, and spring brass. The laboratory use of zinc includes preparing hydrogen gas and as a reducing agent in a number of chemical reactions. Zinc salts have numerous uses (See under specific compounds). Zinc is an essential nutrient element required for growth of animals.

Physical Properties

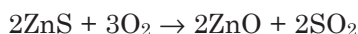
Bluish-white lustrous metal; brittle at room temperature; malleable between 100 to 150°C; hexagonal close-packed structure; density 7.14 g/cm³; melts at 419.6°C; vaporizes at 907°C; vapor pressure 1 torr at 487°C, 5 torr at 558°C and 60 torr at 700°C; good conductor of electricity, electrical resistivity 5.46 microhm-cm at 0°C and 6.01 microhm-cm at 25°C; surface tension 768 dynes/cm at 600°C; viscosity 3.17 and 2.24 centipoise at 450 and 600°C, respectively; diamagnetic; magnetic susceptibility 0.139x10⁻⁶ cgs units in polycrystalline form; thermal neutron absorption cross-section 1.1 barns.

Thermochemical Properties

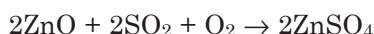
ΔH_f° (cry)	0.0
ΔH_f° (gas)	31.2 kcal/mol
ΔG_f° (gas)	22.7 kcal/mol
S° (cry)	9.94 cal/deg mol
S° (gas)	38.5 cal/deg mol
C_p (cry)	6.07 cal/deg mol
C_p (gas)	4.97 cal/deg mol
ΔH_{fus}	1.75 kcal/mol
Thermal Conductivity (at 27°C)	1.16 W/cm K
Coefficient of linear expansion (at 25°C)	30.2x10 ⁻⁶ /°C

Recovery

Practically all zinc produced today comes from sulfide ores, sphalerite or blende. The ore is first roasted to form zinc oxide. The primary reaction is:

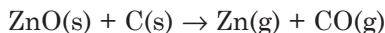


Also, some zinc sulfate is produced in the roasting:



Two methods are employed broadly in producing zinc metal from its oxide.

One is distillation in which roasted zinc oxide is mixed with excess carbon or carbonaceous materials and reduced at elevated temperatures in a furnace.

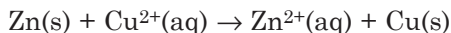


Reduction temperature is usually around 1,300°C. Zinc obtained as vapor is condensed and collected in vessels connected to the reduction retort.

Zinc also may be produced by electrolysis of zinc sulfate solution. The zinc oxide in the roasted concentrate is leached with sulfuric acid. The oxide is converted to soluble zinc sulfate. Impurity metals, such as iron, copper, cadmium, arsenic, tin, and cobalt are removed by precipitation, floc formation, and other methods. The purified zinc sulfate solution is electrolyzed using aluminum cathodes and lead anodes. Zinc is deposited on the cathode.

Reactions

Zinc exhibits a valence of +2 in all its compounds. It also is a highly electropositive metal. It replaces less electropositive metals from their aqueous salt solutions or melts. For example, a zinc metal bar put into Cu^{2+} solution acquires a brown-black crust of copper metal deposited on it. At the same time the blue color of the solution fades. Zinc reduces Cu^{2+} ions to copper metal. The overall reaction is:



This spontaneous reaction was used first in 1830 to make a voltaic cell.

The metal is attacked by mineral acids. Reactions with sulfuric and hydrochloric acids produce hydrogen. With nitric acid, no hydrogen is evolved but the pentavalent nitrogen is reduced to nitrogen at lower valence states.

Zinc is attacked by moist air at room temperature. Dry air has no action at ambient temperatures but the metal combines with dry oxygen rapidly above 225°C.

Zinc reacts with carbon dioxide in the presence of moisture at ordinary temperatures forming a hydrated basic carbonate. The metal, on heating with dry halogen gases, yields zinc halides. However, in the presence of moisture the reaction occurs rapidly at ambient temperatures.

The metal dissolves in hot solutions of caustic alkalis to form zincates and evolves hydrogen:



Analysis

Zinc in trace amounts may be measured in solutions by flame-and furnace-AA, ICP-AES, and ICP/MS methods. It also can be identified by x-ray fluorescence and neutron activation analysis. Flame-AA measurement is done at 213.9nm using an air-acetylene flame. The ICP-AES measurement may be done at 213.86 nm or 206.20nm or alternative wavelengths. ICP/MS is the most sensitive method.

Zinc also can be identified in aqueous solutions by colorimetric methods. Two such methods, known as “dithizone” and “zincon” methods are applicable to analyze zinc in water (APHA, AWWA, and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association).

Toxicity

Zinc is an essential nutrient and is not regarded as toxic. However, the metal fumes, its oxide fumes, and chloride fumes can produce adverse inhalation effects. (See Zinc Oxide and Zinc Chloride, Toxicity) Ingestion of soluble salts can cause nausea.

ZINC ACETATE

[557-34-6]

Formula $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$; MW 183.46; takes on water to become a stable dihydrate, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ [5970-45-6], MW 219.51

Uses

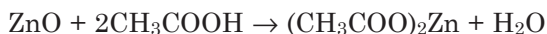
Zinc acetate is used as a mordant in dyeing textiles; in preserving wood; in manufacturing glazes for painting on ceramics; and as an analytic reagent in measuring albumin, tannin, and phosphate. Other uses are as a crosslinking agent for polymers; and as a supplement in food. The compound is used in medicine as an astringent.

Physical Properties

The dihydrate $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ is a white lustrous powder; faint acetic acid odor; astringent taste; monoclinic crystals; density 1.735 g/cm³; loses water at 100°C; decomposes at 237°C; readily dissolves in water, 43g/100 mL at 20°C; soluble in alcohol.

Preparation

Zinc acetate is prepared by the reaction of acetic acid with zinc oxide followed by crystallization (crystals of dihydrate obtained):



Analysis

Water of crystallization is measured by thermogravimetric analysis. An aqueous solution is analyzed for zinc by AA or ICP.

ZINC BROMIDE

[7699-45-8]

Formula ZnBr_2 ; MW 225.19

Uses

Zinc bromide is used in preparing photographic emulsions, and in producing rayon. Concentrated solution is used as a shield in viewing windows for nuclear reactions.

Physical Properties

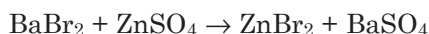
White crystalline powder; sharp metallic taste; orthorhombic structure; refractive index 1.5452; density 4.20 g/cm³; very hygroscopic; melts at 394°C; vaporizes at 650°C; highly soluble in water 447g/100 mL at 20°C; aqueous solution acidic; very soluble in alcohol, ether, and acetone; soluble in alkali hydroxides and ammonia solution.

Thermochemical Properties

ΔH_f° (ZnBr ₂)	-78.55 kcal/mol
ΔH_f° (ZnBr ₂ · 2H ₂ O)	-224.0 kcal/mol
ΔG_f° (ZnBr ₂ · 2H ₂ O)	-191.1 kcal/mol
ΔG_f° (ZnBr ₂)	-74.60 kcal/mol
S° (ZnBr ₂)	33.1 cal/deg mol
S° (ZnBr ₂ · H ₂ O)	47.5 cal/deg mol

Preparation

Zinc bromide is prepared by mixing barium bromide and zinc sulfate solutions. The product barium sulfate is removed by filtration and the filtrate is evaporated to obtain crystals of zinc bromide:



Zinc bromide also may be prepared by the action of zinc with hydrobromic acid followed by crystallization.

Analysis

Elemental composition: Zn 29.03%, Br 70.97%

An aqueous solution is analyzed for zinc metal (see Zinc) by AA, ICP, and other methods, and for Br⁻ by ion chromatography.

ZINC CARBONATE

[3486-35-9]

Formula ZnCO₃; MW 125.39

Occurrence and Uses

Zinc carbonate occurs in nature as mineral smithsonite and zincspar. The compound is used in ceramics and fire proofing filler for rubber and plastics.

Also, it is used in lotions, ointments, cosmetics, and as a topical antiseptic.

Physical Properties

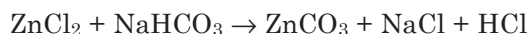
White crystalline solid; orthorhombic structure; refractive index 1.818; Mohs hardness 4.3; density 4.398 g/cm³; decomposes at 300°C forming zinc oxide; practically insoluble in water, 10 mg/L at 15°C; soluble in acids, alkalis, and ammonium salt solutions.

Thermochemical Properties

ΔH_f°	-194.3 kcal/mol
ΔG_f°	-174.8 kcal/mol
S°	19.7 cal/deg mol
C_p	19.05 cal/deg mol

Production

Zinc carbonate is derived from its mineral smithsonite. Also, the compound may be prepared by the reaction of sodium bicarbonate with a soluble zinc salt:



Analysis

Elemental composition: Zn 52.14%, C 9.58%, O 38.28%. Zinc carbonate is identified by effervescence produced upon adding dilute HCl. CO₂ evolved is identified by the lime water test or by GC or GC/MS. Characteristic mass for identification of CO₂ is 44. Zinc may be analyzed in an acid solution by AA, ICP, and other methods to measure zinc content of the compound.

ZINC CHLORIDE

[7646-85-7]

Formula ZnCl₂; MW 136.29

Uses

Zinc chloride is used as a wood preservative and in fireproofing timber. Other uses are as a deodorant in disinfecting fluids; in dental cements; in electroplating; in etching metals and glass; as flux for soldering; as a mordant in printing and dyeing textiles; in making dry batteries; in denaturing alcohols; in vulcanizing rubber; in manufacturing parchment; in making artificial silk; in making activated carbon and cold-water glues; and in refining petroleum. Also, zinc chloride is used as a dehydrating and condensing agent in organic syntheses. In medicine it is used as an astringent and antiseptic.

Physical Properties

White crystalline powder or granules; hygroscopic; density 2.907 g/cm³; melts at 290°C; vaporizes at 732°C; vapor pressure 1 torr at 428°C and 20 torr

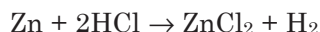
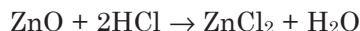
at 536°C; highly soluble in water, 432 g/100mL at 25°C; aqueous solution acidic in litmus test; also soluble in ethanol, glycerol, and acetone.

Thermochemical Properties

ΔH_f° (cry)	-99.2 kcal/mol
ΔH_f° (gas)	-63.6 kcal/mol
ΔG_f° (gas)	-88.3 kcal/mol
S° (cry)	26.6 cal/deg mol
C_p (cry)	17.0 cal/deg mol
ΔH_{fus}	30.1 kcal/mol

Preparation

Zinc chloride is prepared by the reaction of zinc oxide or zinc metal with dilute hydrochloric acid, followed by crystallization:



Analysis

Elemental composition: Zn 47.97%, Cl 52.03%. The compound usually contains small amounts of oxychloride and water. An aqueous solution may be analyzed for zinc by AA, ICP, and other methods (See Zinc), and for chloride ion by titration against a standard solution of silver nitrate using potassium chromate indicator. Chloride ion also may be determined by ion chromatography after sufficient dilution.

Toxicity

Inhalation of zinc chloride fumes can injure lungs and respiratory tract. Dusts or fumes also cause dermatitis, boils, conjunctivitis, and gastrointestinal tract upset (Lewis(Sr), R.J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold).

LD₅₀ oral (rat): 350mg/kg

LC_{LO} (inhalation): 1.960 g/m³/10 min

ZINC CYANIDE

[557-21-1]

Formula Zn(CN)₂; MW 117.42

Uses

Zinc cyanide is used in electroplating; as an insecticide; and for separating ammonia from producer gas.

Physical Properties

White powder; orthorhombic crystals; density 1.852 g/cm³; decomposes at

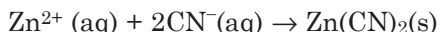
800°C; insoluble in water (about 5mg/L at 20°C); soluble in alkalies, potassium cyanide and ammonia solutions; insoluble in alcohol.

Thermochemical Properties

ΔH_f° 22.9 kcal/mol

Preparation

Zinc cyanide is precipitated by mixing solutions of potassium cyanide and a soluble zinc salt, such as zinc chloride or sulfate:



Analysis

Elemental composition: Zn 55.68%, C 20.46%, N 23.86%. A small and measured amount is treated with dilute sulfuric acid. Hydrogen cyanide generated is swept with a purging gas and collected in sodium hydroxide solution. The solution is analyzed for cyanide by a colorimetric method using pyridine-barbituric acid reagent or by cyanide ion-specific electrode (See Hydrogen Cyanide, Analysis). The acid solution may be analyzed for zinc to measure its content in the compound.

Toxicity

The compound is toxic by oral and intraperitoneal routes. The intraperitoneal lethal dose in rat is 100 mg/kg.

ZINC FLUORIDE

[7783-49-5]

Formula ZnF_2 ; MW 103.39; forms a tetrahydrate, $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ [13986-18-0], MW 175.45

Uses

Zinc fluoride is used in the manufacture of phosphors for fluorescent lights. It also is used in electroplating baths, in preservation of wood, in glazes and enamels for ceramics, and in fluorination reactions of organics.

Physical Properties

Anhydrous zinc fluoride is a white hygroscopic solid; tetragonal needles; density 4.9 g/cm³; melts at 872°C; vaporizes at 1,500°C; vapor pressure 1 torr at 1,243°C and 5 torr at 1,328°C; practically insoluble in water, 5.2 mg/L; sparingly soluble in HCl, HNO₃ and ammonia solution.

The hydrated salt, $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$, is a white crystalline solid; rhombohedral crystals; density 2.30 g/cm³; loses water of crystallization at 100°C; sparingly

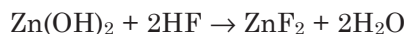
soluble in water, about 1.52 g/100mL at 20°C.

Thermochemical Properties

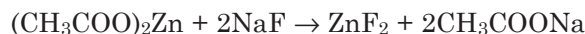
ΔH_f°	-182.7 kcal/mol
ΔG_f°	-170.5 kcal/mol
S°	17.6 cal/deg mol
C_p	15.7 cal/deg mol
ΔH_{vap}	45.4 kcal/mol

Preparation

Zinc fluoride may be prepared by heating zinc hydroxide or zinc carbonate with hydrogen fluoride:



Also, it can be precipitated by adding a solution of sodium fluoride to that of zinc acetate:



Analysis

Elemental composition: Zn 63.24%, F 36.76%. ZnF_2 may be characterized from its x-ray and other physical properties. The water of crystallization in the tetrahydrate may be determined by thermogravimetric method. A small amount of compound is dissolved in water (anhydrous salt is very slightly soluble in water) and analyzed for fluoride ion by the electrode method or by ion chromatography. A diluted acid solution of the compound is analyzed for zinc by various instrumental methods (See Zinc).

ZINC HYDROXIDE

[20427-58-1]

Formula: Zn(OH)_2 ; MW 99.41

Uses

Zinc hydroxide is used in the preparation of other zinc compounds. Another application is as an absorbent in surgical dressings.

Physical Properties

Colorless orthorhombic crystals; density 3.053 g/cm³; decomposes at 125°C; slightly soluble in water.

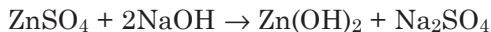
Thermochemical Properties

ΔH_f°	-153.4 kcal/mol
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ΔG_f°	-132.3 kcal/mol
S°	19.4 cal/deg mol

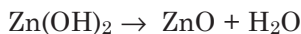
Preparation

The compound is prepared by adding a strong alkali to a solution of zinc sulfate or chloride:



Analysis

Zinc hydroxide is decomposed to form zinc oxide and water; the mass of oxide formed may be determined by gravimetry:



The oxide may be characterized by x-ray diffraction.

The zinc content in the hydroxide may be determined by flame- or furnace AA or by ICP-AES after acid digestion.

ZINC NITRATE

[7779-88-6]

Formula $\text{Zn(NO}_3)_2$; MW 189.40 obtained as hexahydrate, $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [10196-18-6]; MW 297.49; also forms a stable trihydrate, $\text{Zn(NO}_3)_2 \cdot 3\text{H}_2\text{O}$

Uses

The compound is used as a mordant in dyeing and as a latex coagulant. It also is used as an acid catalyst and as an analytical standard for zinc.

Physical Properties

The hexahydrate, $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, is a colorless and odorless crystalline solid; tetragonal structure; density 2.065 g/cm³ at 15°C; melts at 36.4°C; loses all its water of crystallization between 105 to 131°C; very soluble in water, about 184 g/100mL water at 20°C; the aqueous solution acidic, the pH of a 5% solution is about 5.1; also very soluble in alcohol.

The trihydrate, $\text{Zn(NO}_3)_2 \cdot 3\text{H}_2\text{O}$ consists of colorless needles; melts at 45.5°C; very soluble in water, 327 g/100mL at 40°C.

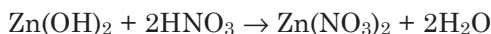
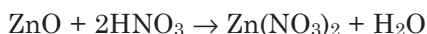
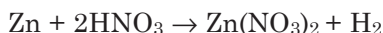
Thermochemical Properties

ΔH_f° [$\text{Zn(NO}_3)_2$]	-115.6 kcal/mol
ΔH_f° [$\text{Zn(NO}_3)_2 \cdot \text{H}_2\text{O}$]	-192.4 kcal/mol
ΔH_f° [$\text{Zn(NO}_3)_2 \cdot 2\text{H}_2\text{O}$]	-265.4 kcal/mol
ΔH_f° [$\text{Zn(NO}_3)_2 \cdot 4\text{H}_2\text{O}$]	-406.1 kcal/mol
ΔH_f° [$\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$]	-551.3 kcal/mol
ΔG_f° [$\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$]	-423.8 kcal/mol

S°	[Zn(NO ₃) ₂ •6H ₂ O]	109.2 cal/deg/mol
C _p	[Zn(NO ₃) ₂ •6H ₂ O]	77.2 cal/deg mol

Preparation

Zinc nitrate is prepared by reacting zinc metal, zinc oxide or zinc hydroxide with nitric acid followed by crystallization. The salt is obtained as hexahydrate:



The salt also is sold commercially in the form of fused pieces and technical flakes containing about 20% and 25.6% water, respectively.

Analysis

Water of crystallization in hydrated salt can be measured by thermogravimetric analysis. Zinc can be measured in an aqueous solution by flame- or furnace- AA or ICP-AES (See Zinc). Nitrate anion can be measured in a diluted solution by ion-selective electrode or by ion chromatography.

ZINC OXIDE

[1314-13-2]

Formula: ZnO; MW 81.38

Synonyms: zinc white; zincite; flowers of zinc

Occurrence and Uses

Zinc oxide occurs in nature as mineral zincite. It is the most important zinc compound and has numerous industrial applications. Zinc oxide is the pigment in white paints. It is used to make enamels, white printing inks, white glue, opaque glasses, rubber products and floor tiles. It is used in cosmetics, soaps, pharmaceuticals, dental cements, storage batteries, electrical equipment, and piezoelectric devices. Other applications are as a flame retardant, as a UV absorber in plastics, and a reagent in analytical chemistry. A major application of zinc oxide is in the preparation of most zinc salts. In medicine, the compound is used as an antiseptic, an astringent and a topical protectant.

Physical Properties

White or yellowish-white powder; odorless; bitter taste; hexagonal crystal; refractive index 2.008; density 5.606 g/cm³; melts at 1,975°C; practically insoluble in water, 1.6 mg/L at about 30°C; soluble in dilute acids, ammonia solu-

tion, and alkali hydroxides.

Thermochemical Properties

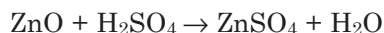
ΔH_f°	-83.24 kcal/mol
ΔG_f°	-76.08 kcal/mol
S°	10.43 cal/deg mol
C_p	9.62 cal deg/mol

Production

Zinc oxide is obtained as an intermediate in recovering zinc from minerals (See Zinc, Recovery). The oxide is prepared by vaporizing zinc metal and oxidation of the zinc vapors with preheated air (French process). The oxide can be produced by other processes. Another method involves roasting franklinite and other ores with coal and then oxidizing the product in air.

Reactions

Zinc oxide reacts with mineral acids to yield corresponding zinc salts when the solution is evaporated. Thus, with sulfuric acid it forms zinc sulfate (hydrated):



Reactions with organic acids such as acetic or propionic acid yields zinc acetate, $(\text{CH}_3\text{COO})_2\text{Zn}$, or zinc propionate, $(\text{CH}_3\text{CH}_2\text{COO})_2\text{Zn}$, upon concentration.

Fusion of zinc oxide with fatty acids at elevated temperatures produces fatty salts. Thus, fusion with oleic or linoleic acid forms zinc oleate, $\text{Zn}(\text{C}_{17}\text{H}_{33}\text{COO})_2$, or zinc linoleate, $\text{Zn}(\text{C}_{17}\text{H}_{31}\text{COO})_2$.

Reaction with tellurium powder in alkaline solution yields red crystalline zinc telluride, ZnTe .

Zinc oxide reacts with potassium dichromate in solution in the presence of sulfuric acid to form a greenish-yellow pigment, zinc yellow or citron yellow [11103-86-9], $4\text{ZnO} \cdot 4\text{CrO}_3 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$

Analysis

Elemental composition: Zn 80.34%, O 19.66%. The oxide is characterized by x-ray diffraction. Zinc content may be measured by dissolving the oxide in nitric acid, diluting and analyzing by AA or ICP (see Zinc).

Toxicity

Exposure to zinc oxide fumes from welding and other operations can cause metal fume fever. Its symptoms are chills, fever, cough, and tightness in the chest.

ZINC SULFATE

[7733-02-0]

Formula: ZnSO_4 ; MW 161.44; forms several hydrates; the commercial product

is heptahydrate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ [7446-20-0], MW 287.56; the monohydrate $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ [7446-19-7], MW 179.47
 Synonyms: white vitriol; zinc vitriol.

Occurrence and Uses

Zinc sulfate occurs in nature as the mineral, zinkosite. The heptahydrate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is the mineral, goslarite. The salt is used as a mordant in calico-printing, in making rayon, in preserving wood, in animal feeds, in electroplating, and in preparing many zinc compounds.

Physical Properties

The anhydrous sulfate is a colorless rhombohedral crystalline solid; refractive index 1.658; density 3.54 g/cm³; decomposes at 600°C; soluble in water, methanol, and glycerol.

The heptahydrate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, is a colorless crystalline solid; metallic taste; rhombohedral crystals; effloresces; refractive index 1.457; density 1.957 g/cm³ at 25°C; melts at 100°C; loses all its water molecules at 280°C; decomposes above 500°C; very soluble in water, 96.5 g/100mL at 20°C; soluble in glycerol, 40 g/100 mL; insoluble in alcohol.

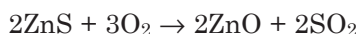
The hexahydrate, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ constitutes colorless monoclinic or tetragonal crystals; density 2.072 g/cm³ at 15°C; loses five water molecules at 70°C; soluble in water.

Thermochemical Properties

ΔH_f° [ZnSO_4]	-234.9 kcal/mol
ΔH_f° [$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$]	-311.8 kcal/mol
ΔH_f° [$\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$]	-663.8 kcal/mol
ΔH_f° [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$]	-735.6 kcal/mol
ΔG_f° [ZnSO_4]	-209.0 kcal/mol
ΔG_f° [$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$]	-270.6 kcal/mol
ΔG_f° [$\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$]	-555.6 kcal/mol
ΔG_f° [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$]	-612.6 kcal/mol
S° [ZnSO_4]	28.6 cal/deg/mol
S° [$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$]	33.1 cal/deg/mol
S° [$\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$]	86.9 cal/deg/mol
S° [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$]	92.9 cal/deg/mol
C_p [$\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$]	85.5 cal/deg mol
C_p [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$]	91.6 cal/deg mol

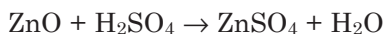
Production

Zinc sulfate is produced as an intermediate in recovering zinc from mineral zinc blende, ZnS (see Zinc, Recovery). The mineral is roasted at about 1,000°C to form zinc oxide and sulfur dioxide which, on prolonged heating in excess air, converts to zinc sulfate:

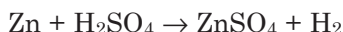




In the zinc recovery process, roasted products are leached with sulfuric acid, whereupon zinc oxide is converted to sulfate.



Also, zinc sulfate can be prepared by reacting metallic zinc with dilute sulfuric acid followed by evaporation and crystallization:



Analysis

Water of crystallization in hydrated salts can be measured by thermogravimetric analysis. Zinc can be analyzed in an aqueous solution by AA or ICP. Sulfate can be identified by precipitation with barium chloride solution or by ion chromatography. The zinc content in the heptahydrate is determined by AA, ICP and other instrumental methods.

ZINC SULFIDE

[1314-98-3]

Formula ZnS; MW 97.46

Synonym: zinc blende

Occurrence and Uses

Zinc sulfide occurs in nature in two crystalline forms, the minerals, wurtzite, and sphalerite. Sulfide ore is the principal zinc mineral.

The most important use of this compound is as a pigment. As lithopone, a mixture with barium sulfate, it forms a low gloss interior house paint. The pigment, "mineral white" is made by combining zinc sulfide with zinc oxide. Zinc sulfide is incorporated into phosphors to produce luminescence when irradiated with light. It is used in making luminous dials, x-ray and television screens, and fluorescent lights. Also, it is used in making white and opaque glass and as a base for color lakes (which consist of an organic pigment with an inorganic carrier)..

Physical Properties

Zinc sulfide is white to gray-white or pale yellow powder. It exists in two crystalline forms, an alpha (wurtzite) and a beta (sphalerite). The wurtzite form has hexagonal crystal structure; refractive index 2.356; density 3.98 g/cm³; melts at 1,700°C; practically insoluble in water, about 6.9 mg/L; insoluble in alkalis; soluble in mineral acids. The sphalerite form arranges in cubic crystalline state; refractive index 2.368; density 4.102 g/cm³; changes to alpha form at 1,020°C; practically insoluble in water, 6.5 mg/L; soluble in mineral

acids, insoluble in alkalis. When zinc sulfide contains water, it slowly oxidizes to sulfate on exposure to air.

Thermochemical Properties

ΔH_f° [wurtzite]	-46.04 kcal/mol
ΔH_f° [sphalerite]	-49.23 kcal/mol
ΔG_f° [sphalerite]	-48.11 kcal/mol
S° [sphalerite]	13.8 cal/deg mol
C_p [sphalerite]	11.0 cal/ deg mol

Production

Zinc sulfide is mined from natural deposits and concentrated by various processes.

Also, zinc sulfide may be prepared in the laboratory by passing hydrogen sulfide through an aqueous solution of a soluble zinc salt, such as zinc chloride or zinc nitrate. The precipitate is filtered, washed, and dried.

Analysis

Elemental composition: Zn 67.09%, S 32.91%. The compound (or the minerals) may be identified by x-ray methods and from their physical properties. The zinc content may be analyzed by AA or ICP-AES in an acid solution.

ZINC THIOCYANATE

[557-42-6]

Formula $\text{Zn}(\text{SCN})_2$; MW 181.56

Synonyms: zinc sulfocyanate; zinc rhodanide

Uses

Zinc thiocyanate is an analytical reagent. Other applications are dyeing of textiles and as a swelling agent for cellulose esters.

Physical Properties

White deliquescent crystals; soluble in water and alcohol; aqueous solution slightly acidic

Preparation

Zinc thiocyanate is prepared by the reaction of ammonium thiocyanate with zinc hydroxide

Analysis

The aqueous solution is analyzed for zinc by AA or ICP-AES. Thiocyanate

ion can be determined by ion chromatography.

ZIRCONIUM

[7440-67-7]

Symbol Zr; atomic number 40; atomic weight 91.224; a Group IVB (Group 4) element of titanium group; a transition metal; electron configuration $[\text{Kr}]4d^25s^2$; valence states, +2, +3, +4; most stable valence +4; atomic radius 1.60Å; ionic radius, Zr^{4+} in crystal 0.84Å for coordination number 8; standard electrode potential, E° for $\text{Zr}^{4+} + 4e^- \leftrightarrow \text{Zr}$ is -1.45V ; five naturally occurring isotopes; Zr-90 (51.45%), Zr-91 (11.22%), Zr-92 (17.15%), Zr-94 (17.38%), Zr-96 (2.80%); twenty-one artificial radioactive isotopes in the mass range 80-89, 93, 95, 97-105; longest-lived radioisotope, is the beta-emitter Zr-93, $t_{1/2}$ 1.5×10^6 years; shortest-lived radioisotope Zr-105, $t_{1/2}$ 1 sec.

History, Occurrence and Uses

Klaproth discovered zirconium oxide in 1789 while investigating a semi-precious gemstone mined in Sri Lanka. The gemstone was a modification of the mineral zircon. Klaproth named the element zirconium from the Arabic word *zargun*, meaning gold color. The element was first prepared in an impure form by Berzelius in 1824 by reduction of potassium zirconium fluoride, K_2ZrF_6 with potassium. Lely and Hamburger in Germany produced high purity zirconium in 1914 by reducing resublimed zirconium tetrachloride, ZrCl_4 , with highly pure sodium. Very pure metal was produced by van Arkel and de Boer in 1925 by decomposition of zirconium iodide, ZrI_4 .

Zirconium is found in small amounts widely spread throughout nature, occurring in many alluvial deposits of lake and stream beds and ocean beaches. The most important mineral is zircon, or zircon orthosilicate, ZrSiO_4 . Other zirconium minerals are eudialite, $(\text{Na}, \text{Ca}, \text{Fe})_6\text{ZrSi}_6\text{O}_{18}(\text{OH}, \text{Cl})$, and baddeleyite, ZrO_2 . It also occurs in monazite sand. The abundance of zirconium in the earth's crust is estimated as 165 mg/kg.

The most important applications of zirconium involve its alloys, Zircaloy. The alloy offers excellent mechanical and heat-transfer properties and great resistance to corrosion and chemical attack. This, in conjunction with the fact that zirconium has a low neutron absorption cross section, makes this alloy a suitable choice as a construction material for thermal nuclear reactors and nuclear power plants. Other uses are as an ingredient of explosive mixtures, as "getter" in vacuum tubes, and in making flash bulb, flash powder (historical), and lamp filaments, in rayon spinnerets, and in surgical appliances.

Physical Properties

Silvery gray lustrous metal or bluish black amorphous powder; close-packed hexagonal lattice; transforms to a body-centered cubic structure at 865°C ; density 6.506 g/cm^3 ; melts at about $1,852^\circ\text{C}$; vaporizes at $4,377^\circ\text{C}$; elec-

trical resistivity 38.8 and 42.9 microhm-cm at 0°C and 25°C, respectively; Young's modulus, annealed 11.35×10^6 psi; shear modulus 5.42×10^6 psi; Poisson's ratio 0.33; magnetic susceptibility 1.55×10^{-6} cgs units at 1,000°K; thermal neutron absorption cross section 0.18 barns; insoluble in water; slightly soluble in acids (solubility varies, see under Reactions); soluble in hydrofluoric acid and aqua regia.

Thermochemical Properties

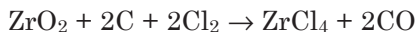
ΔH_f° (cry)	0.0
ΔH_f° (gas)	145.5 kcal/mol
ΔG_f° (cry)	0.0 kcal/mol
ΔG_f° (gas)	135.4 kcal/mol
S° (cry)	9.32 cal/deg mol
S° (gas)	43.3 cal/deg mol
C_p (cry)	6.06 cal/deg mol
C_p (gas)	6.37 cal/deg mol
ΔH_{fus}	5.02 kcal/mol
Thermal conductivity(at 27°C)	0.227 W/cm K
Coefficient of linear expansion, at 25°C	$5.7 \times 10^{-6}/^\circ\text{C}$

Recovery

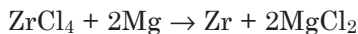
The metal is most often recovered from its principal ore, zircon. The ore is mined, crushed and preliminary segregation is by gravity, electrostatic, and magnetic separation. Separated ore mixed with carbon is charged into an arc furnace and heated to about 3,500°C. This forms zirconium carbide and silicon monoxide, and the monoxide is driven off as vapor. Zirconium carbide is then placed in a chlorinator and heated with chlorine gas at high temperatures. The carbide is converted to zirconium tetrachloride, ZrCl_4 . Also, small amounts of hafnium that is always associated with zirconium converts to its tetrachloride, HfCl_4 .

The crude tetrachloride mixture of zirconium and hafnium is dissolved in ammonium thiocyanate solution. The solution is extracted with methyl isobutyl ketone (MIBK). MIBK is passed countercurrent to aqueous mixture of tetrachloride in the extraction column. Hafnium is preferentially extracted into MIBK leaving zirconium in the aqueous phase. Simultaneously, zirconium tetrachloride oxidizes to zirconyl chloride, ZrOCl_2 . When sulfuric acid is added to aqueous solution of zirconyl chloride, the chloride precipitates as a basic zirconium sulfate. On treatment with ammonia solution the basic sulfate is converted into zirconium hydroxide, $\text{Zr}(\text{OH})_4$. Zirconium hydroxide is washed, dried, and calcined to form zirconium oxide, ZrO_2 .

Zirconium metal is produced from its tetrachloride by reduction with magnesium by the Kroll process. The oxide obtained above is converted to zirconium tetrachloride by heating with carbon and chlorine. In practice, the oxide is mixed with lampblack, powdered sugar, and a little water, and pelletized. The dried pellet is then heated with chlorine in a chlorinator to produce zirconium tetrachloride:



The Kroll process involves heating molten magnesium and zirconium tetrachloride vapor in a sealed furnace in the absence of air under a helium atmosphere. The reaction forms zirconium sponge and magnesium chloride:



Magnesium chloride and excess magnesium are removed by distillation at reduced pressure. Pure zirconium may be prepared by several methods that include iodide decomposition process, zone refining, and electron beam melting. Also, Zr metal may be electrorefined in a molten salt bath of potassium zirconium fluoride, K_2ZrF_6 .

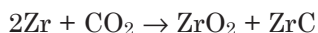
Reactions

Zirconium exhibits quadrivalency in most of its compounds although divalent and trivalent compounds also exist. Zirconium reacts with oxygen to form zirconium oxide, ZrO_2 . In powder form, Zr metal ignites spontaneously forming oxide. Solid metal, however, is stable in air at ordinary temperatures, but reacts slowly at 200°C. Reaction is rapid at high temperatures.

Reaction with hydrogen occurs at temperatures of 300 to 1,000°C forming a brittle dihydride, ZrH_2 . Zirconium combines with halogens at high temperatures forming tetrahalides. Reactions occur in the range 200 to 400°C. Solid tetrahalides sublime above 300°C.

Zirconium combines with nitrogen at 400°C. The reaction becomes rapid above 800°C. The product is zirconium nitride, ZrN . Some nitrogen also dissolves in the metal forming a solid state solution. Zirconium at elevated temperatures combines with most other nonmetals forming binary compounds, including sulfur, phosphorus, and carbon. Although stable to most acids, the metal is attacked by concentrated hydrochloric and sulfuric acids under boiling conditions, aqua regia, and hydrofluoric acid. The metal is stable in organic acids under all conditions. Also, the metal is stable to caustic alkalies.

The metal reacts rapidly with carbon dioxide above 1,000°C forming zirconium oxide and zirconium carbide:



A similar reaction occurs with carbon monoxide above 800°C forming zirconium oxide and carbide.

Analysis

The metal can be analyzed by several instruments including flame-AA, ICP-AES, ICP-MS, and x-ray fluorescence. Also, it can be detected by neutron activation analysis.

ZIRCONIUM CARBIDE

[12020-14-3]

Formula: ZrC; MW 103.235

Uses

Zirconium carbide is a refractory material. It is used in making incandescent filaments, high temperature electrical conductors, and cutting tool components.

Physical Properties

Gray metallic solid; cubic structure; very hard, hardness > 8.0 Mohs; density 6.73 g/cm³; melts at 3,532°C; insoluble in water; slightly soluble in concentrated sulfuric acid; soluble in hydrofluoric acid and oxidizing acids, such as nitric and perchloric acids; attacked by oxidizers

Thermochemical Properties

ΔH_f°	-48.5 kcal/mol
ΔG_f°	-47.7 kcal/mol
S°	7.96 cal/deg mol
C_p	9.06 cal/deg mol

Preparation

Zirconium carbide is prepared by heating a mixture of zirconium oxide and coke in an arc furnace.

Analysis

Zr carbide is digested with nitric and perchloric acid. The solution is diluted and analyzed for zirconium by AA or ICP-AES. Also, the carbide may be identified by x-ray diffraction.

ZIRCONIUM HYDRIDE

[7704-99-6]

Formula: ZrH₂; MW 93.24

Uses

Zirconium hydride is a "getter" in vacuum tubes. The compound is a powerful reducing agent in acid solution or at high temperatures. Also, it is used as a source of pure hydrogen and a catalyst in hydrogenation reactions. Some other applications are in powder metallurgy; as a moderator in nuclear reactors; and as a metal-foaming agent.

Physical Properties

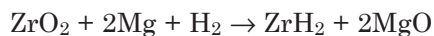
Grayish-black powder; density 5.60 g/cm³; stable in water; soluble in dilute hydrofluoric acid; soluble in concentrated acids.

Thermochemical Properties

ΔH_f°	-40.4 kcal/mol
ΔG_f°	-30.8 kcal/mol
S°	8.37 cal/deg mol
C_p	7.40 cal/deg mol

Preparation

Zirconium hydride may be prepared by heating zirconium oxide with magnesium in the presence of hydrogen:



Alternatively, hydride may be made by heating zirconium oxide with calcium hydride in the presence of hydrogen.

Hydride also may be obtained by combining zirconium metal with hydrogen at elevated temperature.

Analysis

Elemental composition: Zr 97.84%, H 2.16%. The compound may be dissolved in concentrated hydrochloric acid, diluted, and analyzed for zirconium (See Zirconium).

ZIRCONIUM HYDROXIDE

[14475-63-9]

Formula: $\text{Zr}(\text{OH})_4$; MW 159.25

Uses

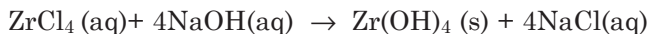
Zirconium hydroxide is used in glass colorants. The compound also is used to prepare zirconium oxide, sulfate, phosphate, and other salts.

Physical Properties

White, bulky amorphous powder; density 3.25 g/cm³; decomposes to oxide at about 500°C; very slightly soluble in water, about 200 mg/L at 20°C; soluble in mineral acids

Preparation

Zirconium hydride precipitates on adding sodium hydroxide solution to an aqueous solution of zirconium salt:



Reactions

When heated at 550°C the hydroxide decomposes to oxide:



Reactions with mineral acids followed by crystallization forms corresponding zirconium salts. Thus hydrochloric, sulfuric, and phosphoric acids yield chloride, sulfate and phosphate of zirconium respectively.

Analysis

Elemental composition: Zr 57.28%, H 2.53%, O 40.19%. The compound is dissolved in acid and analyzed for zirconium (See Zirconium). Hydroxide is heated at about 550°C and residual ZrO_2 is measured by gravimetry. Also, the oxide formed may be identified by x-ray diffraction.

ZIRCONIUM NITRATE

[13746-89-9]

Formula: $\text{Zr}(\text{NO}_3)_4$; MW 339.25; obtained as pentahydrate, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, MW 429.32

Uses

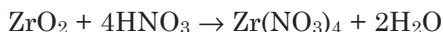
Zirconium nitrate is used as a preservative, as an analytical standard for zirconium, and in making zirconium salts

Physical Properties

The pentahydrate is a white crystalline solid; very hygroscopic; refractive index 1.60; very soluble in water; the aqueous solution acidic; soluble in alcohol

Preparation

Zirconium nitrate is prepared by reacting nitric acid with zirconium oxide:



The compound is crystallized as pentahydrate following evaporation to dryness.

Analysis

Elemental composition (for anhydrous $\text{Zr}(\text{NO}_3)_4$: Zr 26.89%, N 16.51, O 56.59%. The water of crystallization can be measured by thermogravimetric methods. The nitrate ion can be measured by ion-selective electrode or ion chromatography. Zirconium may be analyzed in an aqueous solution by flame

AA or ICP-AES (See Zirconium).

ZIRCONIUM OXIDE

[1314-23-4]

Formula: ZrO_2 ; MW 123.22

Synonyms: zirconia; zirconium dioxide; zirconic anhydride

Occurrence and Uses

Zirconium oxide occurs in nature as the mineral baddeleyite. The oxide has many industrial applications. It is used as a refractory material. It is used in making highly reflective glazes for ceramics, glasses, linings of metallurgical furnaces, crucibles, and laboratory equipment. The oxide is used to produce oxyhydrogen and incandescent lights. Other uses are in producing piezoelectric crystals, heat-resistant fibers, and high-frequency induction coils. The hydrous oxide is used in treating dermatitis resulting from poison ivy.

Physical Properties

White, heavy, amorphous powder or monoclinic crystals; refractive index 2.13; density 5.68 g/cm³; Mohs hardness 6.5; transforms to tetragonal structure above 1,100°C and cubic form above 1,900°C; melts at 2,710°C and vaporizes at about 4,300°C; insoluble in water; soluble in hydrofluoric acid and hot sulfuric, nitric and hydrochloric acids.

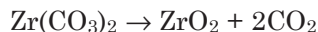
Thermochemical Properties

ΔH_f°	-263.0 kcal/mol
ΔG_f°	-249.2 kcal/mol
S°	12.0 cal/deg mol
C_p	13.4 cal/deg mol
ΔH_{fus}	20.8 kcal/mol

Production

Zirconium oxide occurs in nature as mineral baddeleyite. Ore is mined from natural deposits and subjected to concentration and purification by various processes. The oxide, however, is more commonly obtained as an intermediate in recovering zirconium from zircon, ZrSiO_4 (See Zirconium, Recovery).

Also, the oxide may be prepared in the laboratory by thermal decomposition of zirconium hydroxide or zirconium carbonate:

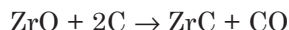


Reactions

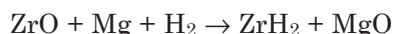
Zirconium oxide combines with silica when heated in an arc furnace producing zirconium silicate, ZrSiO_4 :



Zirconium oxide is reduced by carbon when heated in a arc furnace, forming zirconium carbide

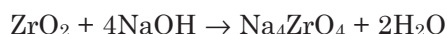


Zirconium oxide is reduced to hydride when heated with magnesium in the presence of hydrogen:



Reaction with nitric acid forms zirconium nitrate and with hydrochloric acid, zirconyl chloride, ZrOCl_2 , is produced.

Fusion with caustic soda at high temperatures forms water-soluble sodium zirconate:



Analysis

Elemental composition: Zr 74.03%, O 25.97%. Oxide may be identified by x-ray diffraction. Zirconium content in the oxide may be measured by analyzing an acid extract by flame AA or ICP-AES.

ZIRCONIUM SILICATE

[10101-52-7]

Formula: ZrSiO_4 ; MW 183.31

Synonyms: zircon; hyacinth; zirconium orthosilicate

Occurrence and Uses

Zirconium silicate occurs in nature as mineral zircon [14940-68-2], the principal source of zirconium. It is used in producing metallic zirconium and its oxide. Other uses are in refractories; glazes; porcelain; enamels; cements; coatings for casting molds; in fritted glass filters; foundry cores; and polishing materials. Also, it is used as a stabilizer for silicon rubbers; and as a catalyst in producing alkyl hydrocarbons. The compound in certain forms is used as gemstone.

Physical Properties

Colorless tetragonal crystals (when pure); presence of impurities forms various colors; density 4.56 g/cm^3 ; hardness 7.5 Mohs; dissociates to ZrO_2 and SiO_2 above $1,540^\circ\text{C}$; melts at $2,550^\circ\text{C}$; insoluble in water, acids, aqua regia, and alkalis; inert in most chemicals

Thermochemical Properties

ΔH_f°	-486.0 kcal/mol
ΔG_f°	-458.7 kcal/mol
S°	20.1 cal/deg mol
C_p	23.58 cal/deg mol

Production

Zirconium silicate occurs in nature as mineral zircon. Ore is mined from natural deposits and concentrated by various techniques (See Zirconium, Recovery). It is separated from sand by electrostatic and electromagnetic methods.

Also, the compound can be made by fusion of SiO_2 and ZrO_2 in an arc furnace, or by reacting a zirconium salt with sodium silicate in aqueous solution.

Analysis

The compound is identified by physical and x-ray diffraction methods.

ZIRCONIUM SULFATE

[14644-61-2]

Formula: $\text{Zr}(\text{SO}_4)_2$; MW 283.34; forms a stable tetrahydrate, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [7446-31-3], MW 355.41

Uses

Zirconium sulfate is used in tanning white leather, as a catalyst support, to precipitate proteins and amino acids, and as a pigment stabilizer.

Physical Properties

Anhydrous sulfate is a microcrystalline hygroscopic solid; density 3.22 g/cm³; decomposes at 410°C; soluble in water.

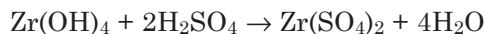
The tetrahydrate, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, is a white crystalline solid; orthorhombic crystals; loses three molecules of water between 100 and 150°C; becomes anhydrous at 380°C; soluble in water, 52.5 g/100g solution; the solution deposits a solid on standing; the aqueous solution is strongly acidic, decomposed by bases or on heating.

Thermochemical Properties

ΔH_f° [$\text{Zr}(\text{SO}_4)_2$]	-529.9 kcal/mol
ΔH_f° [$\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$]	-610.4 kcal/mol
ΔH_f° [$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$]	-825.6 kcal/mol
C_p [$\text{Zr}(\text{SO}_4)_2$]	41 cal/deg mol

Preparation

Zirconium sulfate is prepared by the action of sulfuric acid on zirconium hydroxide:



Also, it is prepared by treating zirconyl chloride with hot concentrated sulfuric acid:



Crystallization forms zirconium tetrahydrate.

Analysis

Water of crystallization may be measured by thermogravimetry. Zirconium may be analyzed in an aqueous solution by flame AA or ICP-AES. Sulfate may be identified in an aqueous solution by ion chromatography or by precipitation with barium chloride.

ZIRCONIUM TETRACHLORIDE

[10026-11-6]

Formula: ZrCl_4 ; MW 233.035

Synonym: zirconium chloride

Uses

Zirconium tetrachloride is used as a Friedel-Crafts catalyst and as a component of Ziegler-type catalysts. It serves as a starting material for producing many zirconium salts and organozirconium compounds. Other uses are in making water-repellent agents for textiles and fibrous materials, tanning agents, and in making zirconium metal.

Physical Properties

White monoclinic crystals; hygroscopic; density 2.80 g/cm³; sublimates at 331°C; triple point 437°C; vapor pressure 1 torr at 190°C; critical temperature 504.85°C; critical pressure 56.95 atm; critical volume 319 cm³/mol; decomposed by water; soluble in alcohol, ether, and concentrated hydrochloric acid.

Thermochemical Properties

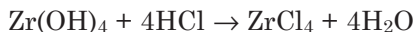
ΔH_f°	-234.3 kcal/mol
ΔG_f°	-212.7 kcal/mol
S°	43.4 cal/deg mol
C_p	28.6 cal/deg mol
ΔH_{fus}	11.95 kcal/mol

Preparation

Zirconium tetrachloride is obtained as an intermediate in recovering zirconium metal from zircon and other minerals (See Zirconium, Recovery). The tetrachloride is obtained by heating a mixture of zirconium hydroxide and car-

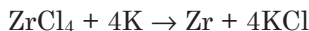
bon with chlorine gas.

Also, tetrachloride can be made by reacting zirconium hydroxide with hydrochloric acid:

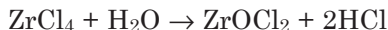


Reactions

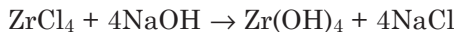
Zirconium tetrachloride is reduced by heating with sodium, potassium or magnesium at high temperatures. Such reduction of tetrachloride has been the commercial method of producing zirconium metal:



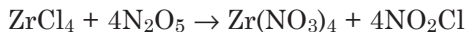
Zirconium tetrachloride decomposes in water forming zirconium oxychloride and hydrochloric acid:



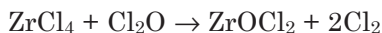
Reaction with sodium hydroxide solution forms zirconium hydroxide:



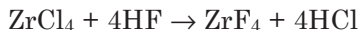
Reaction with dinitrogen pentoxide yields zirconium nitrate:



Reaction with chlorine oxide forms zirconium oxychloride:



Reaction with hydrofluoric acid yields zirconium tetrafluoride:



Analysis

Elemental composition: Zr 39.14%, Cl 60.86%. The compound is decomposed in water to ZrOCl_2 and HCl . A portion is analyzed for zirconium (see Zirconium). Another portion is measured for chloride and oxychloride ions by ion chromatography.

ZIRCONYL CHLORIDE

[7699-43-6]

Formula: ZrOCl_2 ; MW 178.13; obtained as octahydrate, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ [13520-92-8], MW 322.25

Synonyms: zirconium oxychloride; basic zirconium chloride; dichlorooxozirconium

Uses

Zirconyl chloride is used to make pigment toners and improve properties of color lakes of acid and basic dyes. Also, it is used to prepare body deodorants and antiperspirant, water repellant, dye precipitant, catalysts, and many zirconium compounds.

Physical Properties

The octahydrate is a white silky solid; tetragonal crystals consisting of tetramers; effloresces; refractive index 1.552; density 1.91 g/cm³; loses six water molecules at 150°C; becomes anhydrous at 210°C; decomposes at 400°C; soluble in water; aqueous solution acidic; also soluble in alcohol and ether; slightly soluble in hydrochloric acid

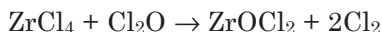
Thermochemical Properties

$$\Delta H_f^\circ \text{ (aq)} \quad -280.3 \text{ kcal/mol}$$

Preparation

The compound is prepared by dissolving zirconium tetrachloride, ZrCl₄, or sodium zirconate, Na₄ZrO₄, in hydrochloric acid solution followed by evaporation to obtain crystals of octahydrate.

Also, the compound can be prepared by reacting zirconium tetrachloride with chlorine oxide:



Analysis

Elemental composition (anhydrous ZrOCl₂): Zr 51.21%, Cl 39.81%, O 8.98%. The compound is dissolved in water and analyzed for zirconium (See Zirconium). The aqueous solution may be analyzed for oxychloride anion by ion chromatography.

Toxicity

Moderately toxic by ingestion, intraperitoneal and subcutaneous routes.

LD₅₀ (intraperitoneal) (rat): 400mg/kg